9. The whole of the measurements given are in agreement with the general theory that the absorption band of the ketones is due to the electromagnetic field of the carbonyl group as influenced by the substituents in the immediate neighbourhood.

The author desires to express his sincere thanks to Prof. E. C. C. Baly for much advice and assistance during the course of the research and for facilities for carrying out the work, also to Dr. A. W. Titherley for advice on the purification of the ketones.

Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.—II.

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§ 1. *Introduction.*

This paper is in continuation of a former one.*

It has been observed by Stark,† and subsequently by Matthies‡ and Child,‖ that a luminous jet of mercury vapour, distilling away from the arc *in vacuo*, into a region quite remote from the electric field of the arc itself, may be deprived of its luminosity by an independent electric field.

The present paper describes experiments made to elucidate this effect in the case of mercury, and similar observations made upon other metallic vapours.

§ 2. *Experiments with Mercury. Electrical Condition in the Luminous Jet.*

Fig. 1 shows a form of apparatus suitable for many of the experiments. The mercury cathode is formed by the top of a barometric column, *a*, connected at the bottom to a rubber tube and reservoir (not shown). The hollow iron tube *b*, 5 mm. internal diameter and about 1 cm. long, forms the anode. It does not touch the glass walls, but is supported on an iron

* 'Roy. Soc. Proc.,' A, vol. 90, p. 364 (1914).
† 'Ann. d. Phys.,' vol. 14, p. 530 (1904).
‡ 'Verh. d. Deut. Phys. Gesell.,' vol. 12, p. 754 (1910).
‖ 'Phil. Mag.,' vol. 26, p. 906 (1913).

wire screwed into it, as shown. The latter passes out through a cemented joint at *c*.

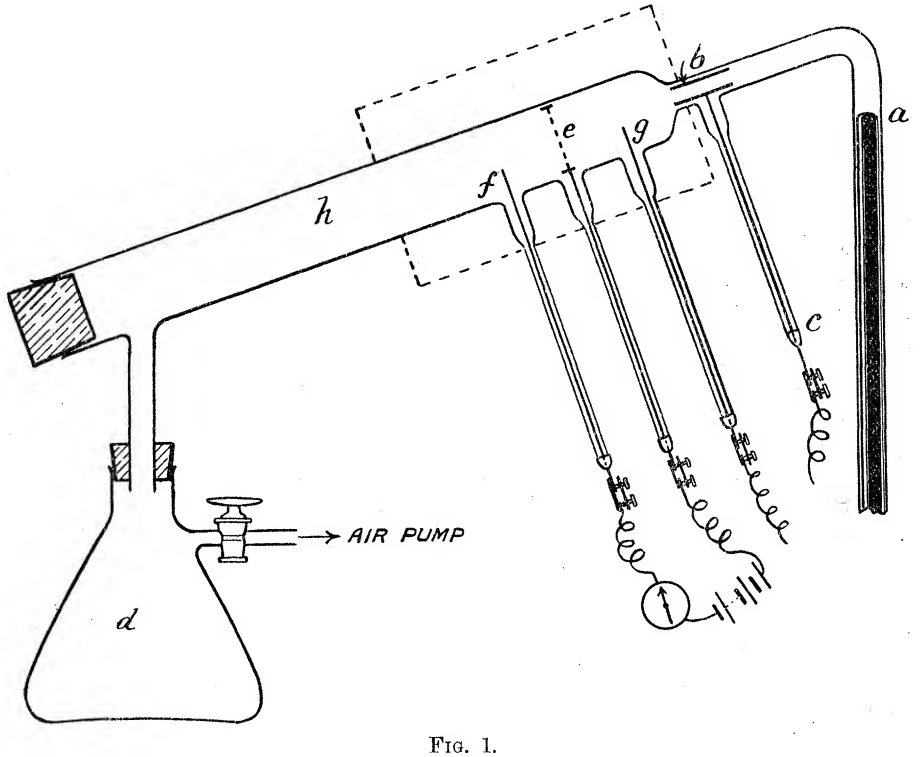

FIG. 1.

In using the apparatus the arc was struck by raising the mercury level and allowing a small quantity of mercury to flow over the bend. A current of about 3 amperes was passed. Mercury vapour distilled down the tube *h*. The upper part of this tube was in an asbestos oven, shown by dotted lines. It was kept hot enough by electric resistance heaters to prevent the mercury from condensing. Further down the mercury was allowed to condense, and fell into the bottle *d*. A Gaede mercury pump attached to the apparatus was kept going continuously. Under these circumstances the vapour passing from *b* through *c* remained luminous until it was condensed.

This general type of apparatus admits of many modifications for different experiments. As shown in fig. 1 the glowing vapour is made to pass through a wire net electrode *e*, consisting of a few fine iron wires stretched across an iron ring;* *e* forms the cathode of an auxiliary circuit distinct from that of the arc, and used for examining the ionisation of the luminous jet. The

* Ordinary wire gauze obstructs the passage of the vapour too much.

anode of this circuit may be an iron wire at f; a current-measuring instrument and a battery of variable E.M.F. are included in it.

With the arrangements described, the current increases with the E.M.F., at first rapidly then more slowly, but it does not appear to attain a very definite limit. Applying, say, 80 volts* between e and f, the current is of the order of 1 or 2 milliampères.

It is remarkable that the value of the current, though very dependent on the shape and position of the cathode, does not depend at all on the form of the anode, or on where it is placed.

For instance, using e as cathode, we may employ either f, or a wire inserted at g, alternatively, as anode, without affecting the current, although f is upstream of the cathode and g downstream of it, in the rapidly moving mercury vapour. If, on the other hand, we use e as anode, the current will be much larger with g as cathode than with f as cathode. A great variety of experiments with different shaped electrodes, which it would be tedious to describe in detail, have always shown that—

(1) With two alternative cathodes of the same shape, a larger current passes when the cathode farther upstream is used.

(2) With a given cathode, the value of the current at any given E.M.F. is independent of the position of the anode.

Experiments made with a testing electrode, or "sound," movable between e and f, and connected to an electrometer, have shown that the fall of potential is almost all in the immediate neighbourhood of the cathode.

It will be observed that the properties of the glowing vapour, regarded as a conductor, are not unlike those of a flame, which is characterised by the great mobility of the negative ions compared with the positive.

We may, I think, interpret the observed facts as follows:—A certain

* If it is attempted to increase the E.M.F. between the auxiliary electrodes very much beyond this, a discharge is set up, giving rise to new luminosity between e and f. This new luminosity is much bluer in colour than that which comes down from the arc in the absence of any E.M.F. If the anode is upstream of the cathode, so that the negative ions moving from cathode to anode have to make their way against the moving stream of mercury vapour, then discharge starts suddenly and capriciously with the passage of a large current. In the opposite case (anode downstream), as the E.M.F. is increased, a patch of blue light begins to appear on the anode and gradually extends towards the cathode. Its appearance is not accompanied by any sudden rise in the current. We may account for this by supposing that the negative ions approaching the anode produce new ions, with luminosity; but that the new positive ions thus produced are unable to make their way upstream against the general movement of the vapour. Thus they are unable to contribute to the current, and have to recombine with the negative ions from which they were originally separated.

When the anode is upstream the case is different, for the negative ions, of great mobility have no difficulty in making their way upstream.

number of positive and negative ions are carried away from the arc by the stream of vapour. Since electricity cannot accumulate indefinitely on the insulated auxiliary circuit, it follows that when a steady state has been reached the number of positive ions carried down from the arc must be equal to the number of negative, at least if we suppose that each ion is monovalent. Some of the positive ions will be removed at the cathode, others will recombine with negative ions. Owing to the much greater mobility of the negative ions the current passing round the circuit essentially depends on the circumstances at the cathode. The number of negative ions removed at the anode cannot exceed the number of positive ones removed at the cathode, however favourably the anode may be presented to the stream of ionised vapour.

Consider the case when the anode is upstream. Since the electric field is only strong near the cathode, the current is not even approximately saturated. By this I mean that extensive recombination is going on in the space between the electrodes. On the other hand, after the moving stream of vapour has carried the positive ions into the strong electric field near the cathode, they are all, or nearly all, removed. This view has been confirmed experimentally by arranging a second pair of electrodes with battery and galvanometer, forming a second auxiliary circuit beyond the gauze cathode. The current in this second auxiliary circuit is reduced to a very small fraction of its original value when the first auxiliary circuit is closed with an E.M.F. of 80 volts. The arrangement is indicated diagrammatically in fig. 2.

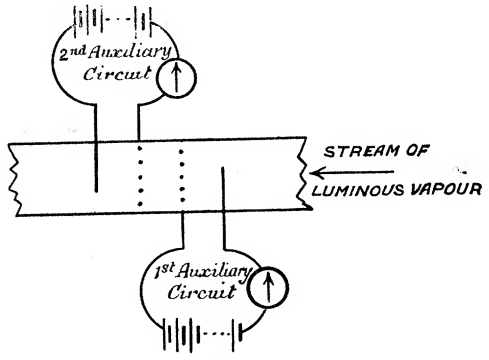

FIG. 2.

§ 3. *Experiments with Mercury. Effect of Electric Field on Luminosity.*

So far we have considered the electrical effects when the auxiliary circuit is closed. Let us now consider the effect on the luminosity of the vapour.

It may be summed up thus: the luminosity is not affected when the

stream of vapour passes the anode, but it is wholly or partially quenched when it passes near the cathode.

The precise effect depends on the particular shape and disposition of the cathode. Using two wire nets at right angles to the stream, with the upstream net as anode, the luminosity passes the anode and extends to within 1 or 2 mm. of the downstream (cathodic) net, at which point it is permanently extinguished. There is, in fact, a small dark space over the cathode, reminiscent of that observed over the cathode of a vacuum discharge, but not, of course, to be in any way identified with it.

If the upstream net is cathode, the extinction occurs a millimetre or two on the upstream side of it as before, and the whole space between the electrodes is dark (fig. 3).

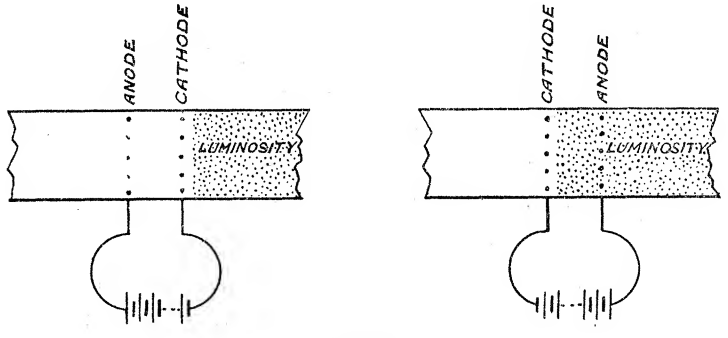

Fig. 3.

Another form of cathode that may be mentioned is a flat plate, several centimetres long, placed parallel to the stream. There is a wedge-shaped dark space over this plate, with its thin end upstream. A cathode consisting of two plates opposite one another, with a metallic connection outside, shows this effect still better (fig. 4). Inside a tubular cathode the luminous stream tapers down similarly.

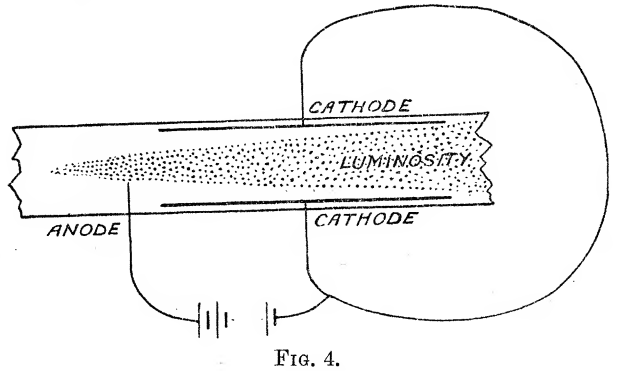

Fig. 4.

It has been emphasised that the current passed in the auxiliary circuit depends on the position and shape of the cathode, but is independent of the position of the anode. Exactly the same applies to the extinction effects. For instance, the stream loses its luminosity in passing through a cathode net whether the anode is upstream or downstream of it.

In the absence of any E.M.F. there is always a considerable loss of light as the stream passes through a net electrode. I have not obtained any distinct evidence as to the cause of this, but the greater luminosity of the stream in front of the obstacle may be simply due to its greater density.

An experiment was arranged in which the luminous stream was symmetrically divided into two, one half of it passing through a glass tube 8 mm. diameter and 3 cm. long, and the other half through an iron tube of exactly the same size. The emerging streams were greatly enfeebled by passing through these comparatively narrow tubes, but the stream from the iron tube was not feebler than the other. Thus there seems no special reason for attributing the enfeeblement to contact of the luminous vapour with a conductor.

§ 4. *Interpretation of the Phenomena. Long Life of the Luminous Centres in the Jet.*

The fact that the luminosity can be at once quenched by removing the positive carriers is consistent with two alternatives. Either (1) the luminous centres are charged, and continue to emit in the charged condition, while they are carried a considerable distance from the arc with the stream of moving vapour; or (2) the actual emission only lasts a very short time, the apparent removal of the luminous centres being really the removal of the positive ions which emit a momentary luminosity during neutralisation. What is removed, on this view, is the raw material from which luminous centres would otherwise be formed.

On the second view, the luminous intensity at any point would be proportional to the rate of recombination there. It would therefore, other things equal, be proportional to the product of the concentrations of the positive and negative ions. This is very difficult to reconcile with an experimental fact that has been mentioned above, namely, that no diminution of luminosity is observed at the anode, when this is the first electrode reached by the luminous stream. Negative ions are, without doubt, removed at the anode, and the concentration of those that remain must be diminished. On the theory (2) the luminosity should be diminished proportionately, and if this theory is to stand at all, we must suppose that the negative ions removed at the anode are an insignificant fraction of the whole number that pass.

The following experiment seems to show that this supposition is not admissible.

Two wire nets, b and c, fig. 5, were arranged across the stream of vapour. Using the first one b as cathode, and the wire a as anode, the current was 2·7 milliampères. As already explained, the removal of positive ions by b was practically complete. Thus the current is a measure of the number of ions that reach this point. Next, using c as cathode and b as anode, the current was found to be diminished to 1·3 milliampère.

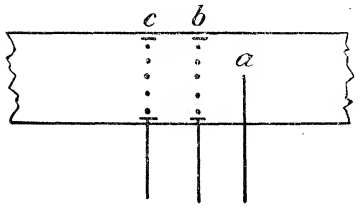

FIG. 5.

It follows, then, that in the absence of a field, the number of positive ions and consequently also the number of negative ones reaching c is about half the number that reach b, the remainder recombining between b and c. If, then, we make c cathode and b anode, we take out as many negative ions at b as we take out positive at c. In other words, under the particular conditions of this experiment, we take out half the entire number of negative ions that reach b, and we reduce by half the rate of recombination at this point. Yet the luminous intensity is not at all affected. It does not appear, therefore, that the luminosity can be attributed to recombination.

We must, then, fall back on the alternative supposition (1), that the luminous centres manufactured in the arc continue to emit light while the vapour travels a considerable distance. We have to suppose that they are charged positively throughout* to account for their removal by passing near a negative electrode.

It is known, from the kinetic theory of gases, that the velocity of the stream of luminous vapour cannot exceed the molecular velocity. Taking, say, 273° as the temperature of the lamp, the molecular velocity of mercury is about 5×10^4 cm. per second. The mercury glow has been observed to travel 50 cm., and might doubtless be made to travel much further. The time for which mercury remains luminous must therefore be at least one thousandth of a second.

Previous writers have considered it impossible that a molecule once set vibrating could remain vibrating so long, and have therefore been driven back on the alternative view that the luminosity is due to the recombination of ions.

* In the case of mercury. We shall see later that in certain other cases there is reason to regard the luminous centres as uncharged.

A calculation by Lorentz* has been cited, which shows that a single electron performing simple harmonic oscillations of wave-length 6×10^{-5} cm. would lose amplitude in the ratio $e:1$ in 4×10^{-8} seconds, and could not therefore travel any appreciable distance before extinction.

But have we adequate reason for considering that the vibrating system is of this character? Even on the older views, it is well known that a system of a few electrons equally spaced round a ring, and revolving uniformly, part with their energy beyond measure less quickly than a single one†; and more recent speculations of Bohr and others, which rest on Planck's conceptions, question whether the mechanism of light vibrations is of this kind at all. It is sometimes suggested that the observed limit of interference shows that the number of vibrations a molecule can execute is limited to a few millions. But another cause, the Döppler effect of the moving molecules, sets a limit to interference.

Bohr's theory of spectrum series, which has excited so much interest, and which has been so successful in its numerical application to certain spectroscopic data, contemplates the sudden jump of an atom (which may or may not be charged) from one state to another with emission of radiation, does not, so far as at present developed, profess to give any account of when, or why, the jump occurs, and cannot therefore set any limit to how long the emission might "hang fire" after the atom has left the place of excitation.

Upon the whole, therefore, it does not seem that we have any very strong grounds at present for calculating how long after excitation an atom may emit light. If not, we cannot decide, upon these grounds, what view is to be taken of the luminous mercury stream. The evidence which has been thought to exclude the theory of recombination as the cause of luminosity has been given above.

§ 5. *Experiments with Various Metals. Some Lines in a Spectrum More Sensitive to Extinction than others. Band Spectra.*

The above experiments made with mercury vapour have been extended to other metals, using the methods described in 'Proc. Roy. Soc.,' A, vol. 90, p. 364, 1914. The general results are similar, but the extension has revealed some new and interesting effects not to be observed with mercury.

The apparatus‡ requires some additions for observing the extinction effects when the glow passes through a negatively electrified wire net. The net *a*

* 'Theory of Electrons,' p. 259 (1909).
† J. J. Thomson, 'Phil. Mag.,' 1903, p. 681.
‡ *Loc. cit.*, p. 365.

(fig. 6) is mounted on a metal rod b passing through a barometric column which admits of its being brought to any desired distance above the jet from which the vapour issues, or being turned out of the way if desired. The anode of the auxiliary circuit may be simply the perforated anode c of the lamp itself from which the luminous vapour issues; or it may be an iron plate d with a hole corresponding to that in c, and insulated from it by the mica washer e. The metal support and contact of d is brought out through the air-pump plate which forms the base of the apparatus with an insulating rubber stopper. The barometric column carrying a is brought out in the same way. The apparatus is covered with a highly exhausted bell-jar as before.

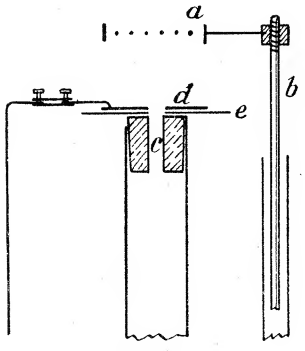

FIG. 6.

In every case examined the line spectra of metals have been observed to be extinguished by passing through the negatively electrified net. The list is as follows:—Sodium, potassium, calcium,* magnesium, mercury, zinc, cadmium, thallium.

The point of chief interest brought out by these experiments is in certain spectra the lines of one series are more easily extinguished than those of another. It is not easy to observe anything of this kind in the case of mercury. But in two cases—sodium and magnesium—it is very conspicuous, and indeed could scarcely escape the attention of anyone making the experiment.

The conditions must not be such as to produce a complete extinction of the whole luminosity, but partial extinction is much more easily achieved than complete extinction, for the latter requires an adjustment of the density of the stream of vapour, dimensions and position of the negatively electrified net, potential applied, etc., which is not in practice nearly so easy to maintain with the metals now under consideration as with mercury.

With sodium, then, if the issuing jet is watched with the spectroscope, it is noticed that on making the auxiliary circuit the D line is far less extinguished than the lines of either of the subordinate series. Several lines of each of these latter series are very conspicuous in the spectrum,

* The difficulty, mentioned in the first paper, of getting a good jet with calcium has been satisfactorily overcome by using, instead of the quartz tube, a tube of quicklime, on which, of course, calcium has no chemical action. The tubes used were drilled out of fine grained marble, and burnt to quicklime afterwards. Only some samples of marble give a coherent quicklime. I believe that fine grain is the essential, but possibly the presence or absence of calcium sulphate, or other impurity, may be important.

and so far as could be observed they all suffered about the same relative diminution of brightness. The small, or in some cases even imperceptible, effect on the D lines was in marked contrast with this. Indeed the difference could be well seen even without the spectroscope, for the greenish luminous jet above the gauze became perceptibly yellower when the key making the auxiliary circuit was depressed.

With magnesium the comparatively faint lines 5712 and 5529 were observed to be very easily extinguished. Next came the blue flame line 4571. The triplet group known as "*b*" (5183), belonging to the subordinate series, was much less affected by the field than any of these.

In some cases the band spectrum of "magnesium hydride" was seen almost as strongly as the line spectrum. This spectrum is more easily extinguished by the field than the triplet *b*. The latter is seen on a background consisting of the bright green band of magnesium hydride. In some experiments this background was most strikingly cleared away from *b* when the circuit was made, leaving the latter almost unaffected.

All these phenomena have at times been seen most strikingly. I must admit, however, that the exact conditions under which they are best brought out are still somewhat obscure. Sometimes it is difficult to get conspicuous extinction effects with any of the magnesium lines, and the appearance or non-appearance of the magnesium hydride bands cannot yet be controlled. The elucidation of these points will no doubt follow with further improvements in technique, which will make prolonged observation easier and diminish the expenditure of time in cleaning, repairing, and recharging the apparatus.

In the zinc spectrum it has been observed that the blue triplet (5182, 4811, 4722) of the subordinate series is distinctly more difficult to quench than the lines 6363, 5310, and 4630. Of these latter, the red line 6363 is much the strongest, and without the spectroscope it can be seen that the light becomes bluer on making the auxiliary circuit, owing to relatively great diminution of the red line.

Similar experiments with cadmium did not show any unmistakable difference in the extinction of the various lines, though it was suspected that the series triplet (5095, 4808, 4682) was less extinguished than other lines.

In the case of mercury, which, to get comparable conditions, was tried in the same apparatus as zinc and cadmium, no indication of any difference between the lines was observed.

Two metals, arsenic and antimony, give luminous jets showing band spectra. The bands are evenly spaced over a considerable region of the spectrum, like

the blue and violet bands of an ordinary nitrogen vacuum tube. After many attempts, I have failed to observe any extinction of these spectra when the auxiliary circuit is made. It would be unwise to build too much on the negative result, for I have occasionally encountered experimental conditions under which the magnesium lines, for instance, were not much extinguished, without understanding clearly what was essential in these conditions. Upon the whole, however, I have very little doubt that the arsenic and antimony spectra are essentially incapable of extinction in this way. Thus, it is natural to assume that the carriers of these particular band spectra are electrically uncharged.

The results obtained in this part of the field are, no doubt, scanty, in comparison with what remains to be done, but they represent a considerable amount of labour, and seem to justify the conclusion that the luminous centres of the principal series in the alkalies are not the same as the luminous centres of the subordinate series. This conclusion is independent of whether we assume, in accordance with the conclusions which have been drawn above, that the centres are excited in the arc, or whether we suppose them to be excited by subsequent neutralisation.

The failure to obtain extinction with the band spectra of arsenic and antimony indicates that no charged particles are concerned in the production of these spectra, and consequently that in these cases, at any rate, the luminosity of the distilled jet cannot be attributed to recombination of ions, and must be excited in the arc itself.

The luminous jets of arsenic and antimony bear so strong a general resemblance to those of the other metals that we cannot reasonably refuse to extend the same conclusion to the latter. This line of argument against the recombination theory of luminosity is independent of that already given, and may be considered confirmatory.

§ 6. *Summary.*

(1) The conducting properties of a luminous jet of mercury vapour distilled from the arc *in vacuo* have been examined. The current depends on the shape and position of the cathode introduced into the jet, and is independent of the position of the anode. In the case where the anode is reached first by the stream of vapour, and a net electrode is used as cathode, all the positive ions may be taken out of the vapour that passes through the cathode. There is saturation of the current in the layer near the cathode. On the other hand, recombination proceeds in the rest of the space between cathode and anode, for the electric force is concentrated near the cathode, and near the anode is not strong enough to take out all the negative ions.

(2) The luminosity of the jet is unaffected by the removal of negative ions at the anode, but is quenched by removal of positive ions at the cathode. Although the removal of negative ions in the former case is not complete, it is considerable enough to show conclusively that the luminosity is independent of the number of negative ions present. Thus the luminosity is not due to recombination of ions. It seems necessary to assume that the luminous centres in the jet are survivors of those generated in the arc itself, in spite of the appreciable time (1/1000 second) necessary for the vapour to travel down the tube. We must suppose these centres to be positively charged to account for their removal at the cathode.

(3) Experimenting with other metals as well as mercury, it is found that the various lines of a spectrum are not, in all cases, equally extinguished when the jet of luminous vapour passes through a negatively electrified net. Thus the lines of the subordinate series of the sodium spectrum apparently all lose intensity in the same ratio; but the D line of the principal series is much less affected. Thus it is inferred that the luminous centres emitting the principal series are not the same as the luminous centres emitting the subordinate series. Analogous differences have been observed in the line spectra of magnesium and zinc.

(4) The jets formed by arsenic and antimony, which show band spectra consisting of large numbers of uniformly spaced bands, are not quenched by passing through a negatively electrified net. The luminous centres appear therefore to be uncharged in these cases. With the band spectrum of magnesium hydride it is otherwise.